Gibbs' Paradox and Non-Uniform Convergence

Chelsea November 1984

ENTROPY OF MIXING

$$\Delta S_{mix} = -R \sum_{i=1}^{M} N_i \ln x_i$$

N_i is no of moles of i^{th} Component

x_i is mole fraction

M is no of Components

For $M=2$, $N_1 = N_2 = 1$

$$\Delta S_{mix} = 2R \ln 2$$

IDEAL MIXTURES

$$\mu_i(T, P, x_i) = \mu_i^*(T, P) + RT \ln x_i$$

μ_i is the <u>chemical potential</u> of the i^{th} component

$$\mu_i \underset{DF}{=} \left.\frac{\partial G}{\partial N_i}\right|_{T, P, N_j}$$

ENTROPY OF PARTIAL SEPARATION

$$\Delta S_{sep}^{(n)}(R)$$

$$= -R\left[\left(1 + E_n(R)\right) \ln\left(1+E_n(R)\right)\right.$$

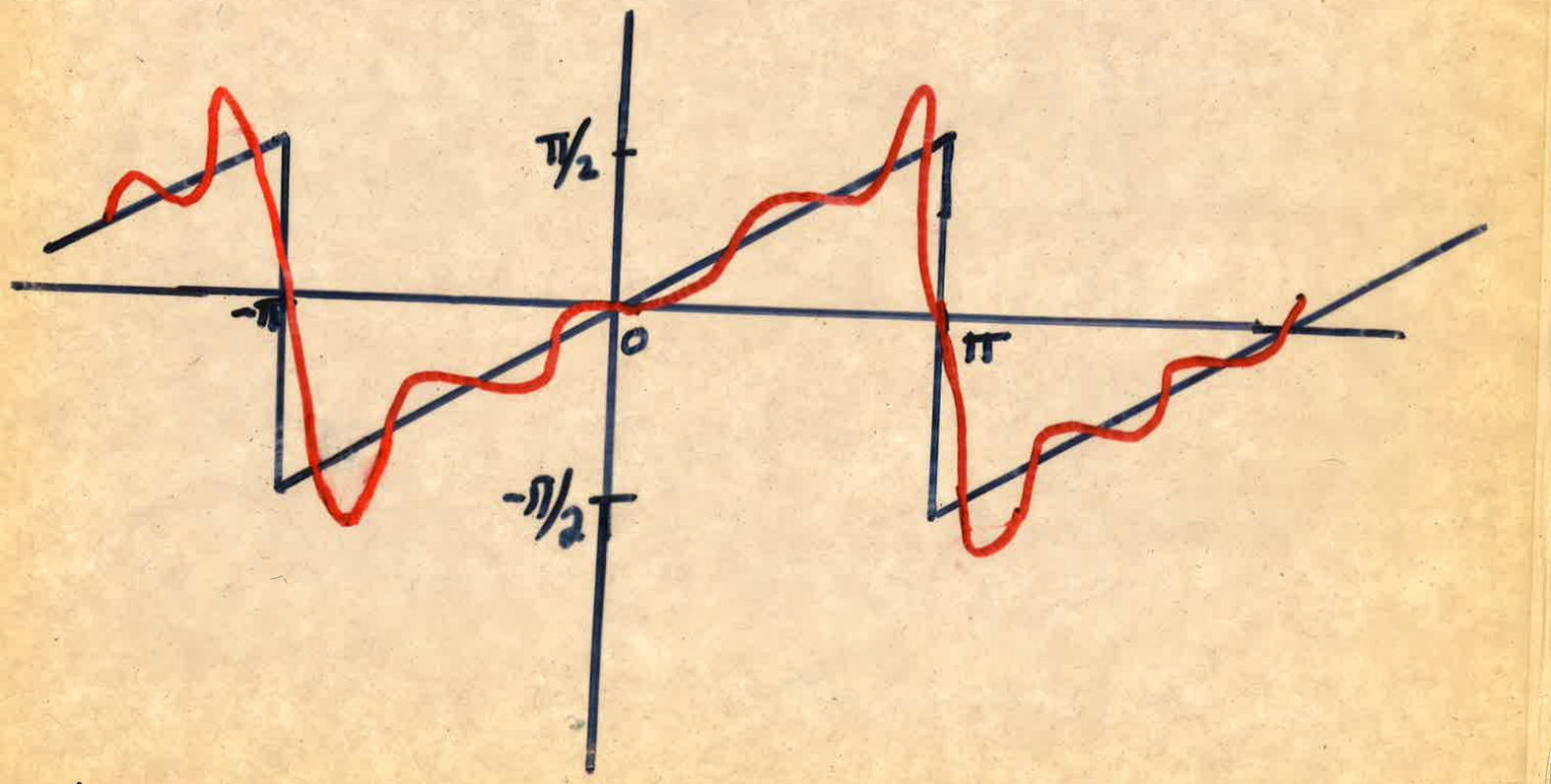
$$\left. + \left(1 - E_n(R)\right) \ln\left(1 - E_n(R)\right)\right]$$

where $E_n(R) = \dfrac{N_A - N_B}{N_A + N_B}$

after the n^{th} stage.

FOURIER SERIES FOR $y = \frac{1}{2}x$

$$\sin x - \frac{1}{2}\sin 2x + \frac{1}{3}\sin 3x \cdots$$



(2)

UNIFORM CONVERGENCE

Sequence $\{S_n(x)\}$ converges uniformly for all x.

$$(\forall \varepsilon > 0)(\exists n)(\forall x)(\forall m > n)$$
$$|S(x) - S_m(x)| < \varepsilon$$

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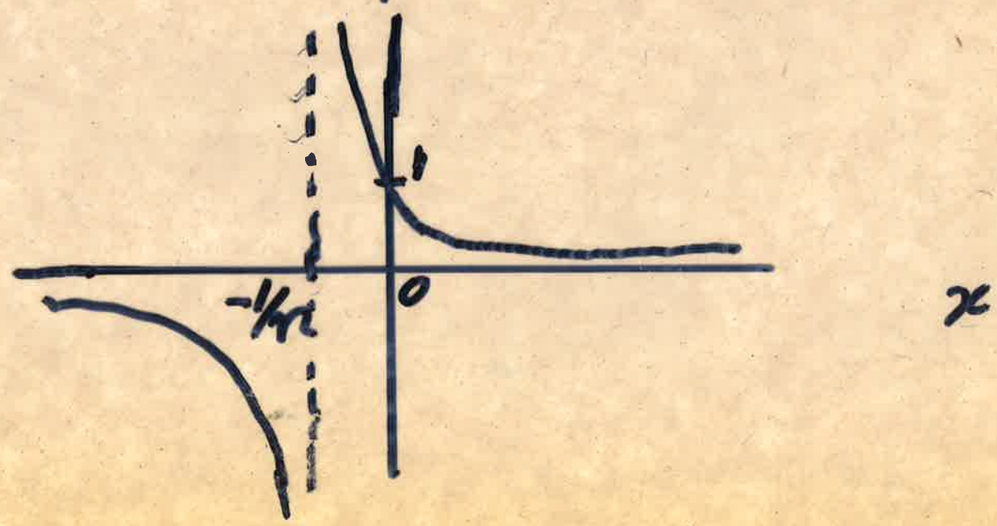
Examples of Non-Uniform Convergence

(1) $S_n(x) = \dfrac{1}{1+nx}$

$x > 0$ $\quad \lim_{n\to\infty} S_n = 0$

$x = 0$ $\quad \lim_{n\to\infty} S_n = 1$

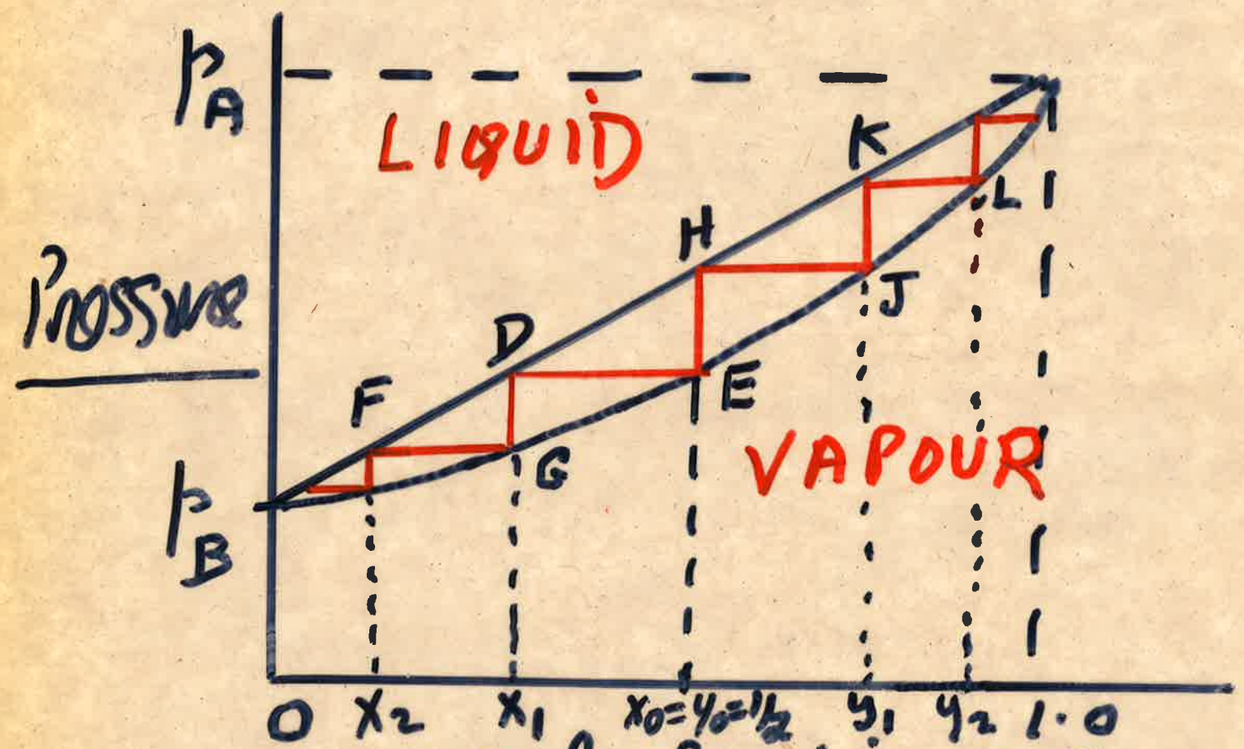


(2) $S_n(x) = \left(\frac{1}{x}\right)^n$

$x > 1 \quad \lim_{n\to\infty} S_n = 0$

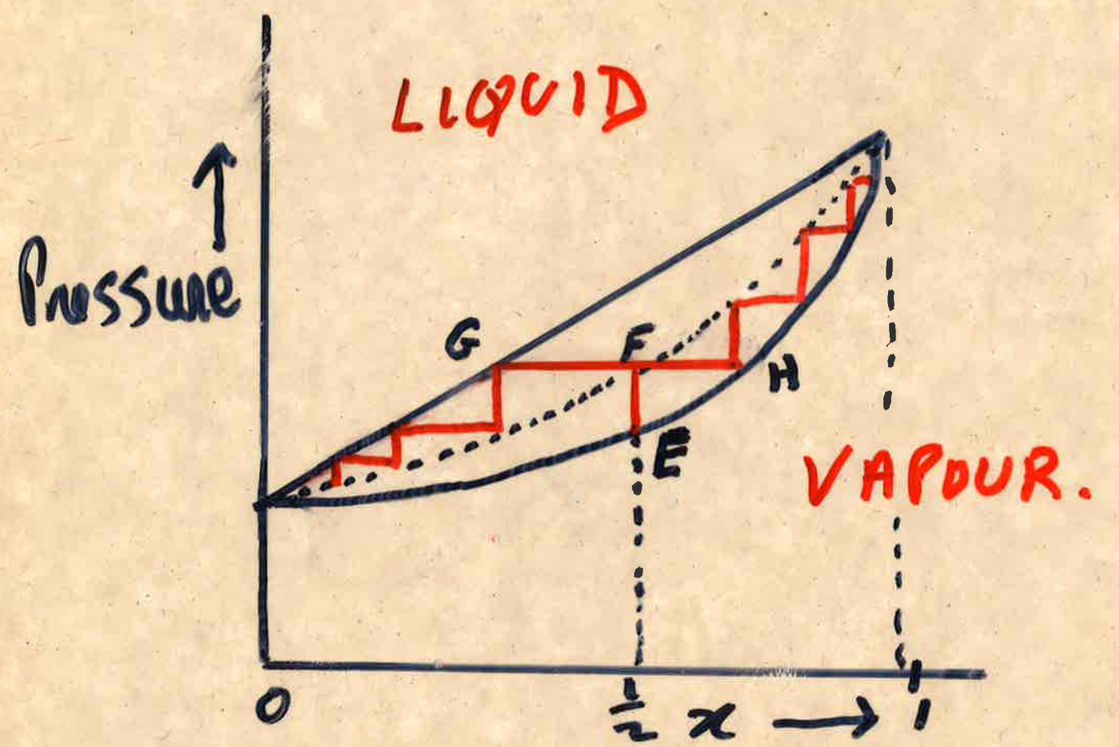
$x = 1 \quad \lim_{n\to\infty} S_n = 1$

FRACTIONAL DISTILLATION

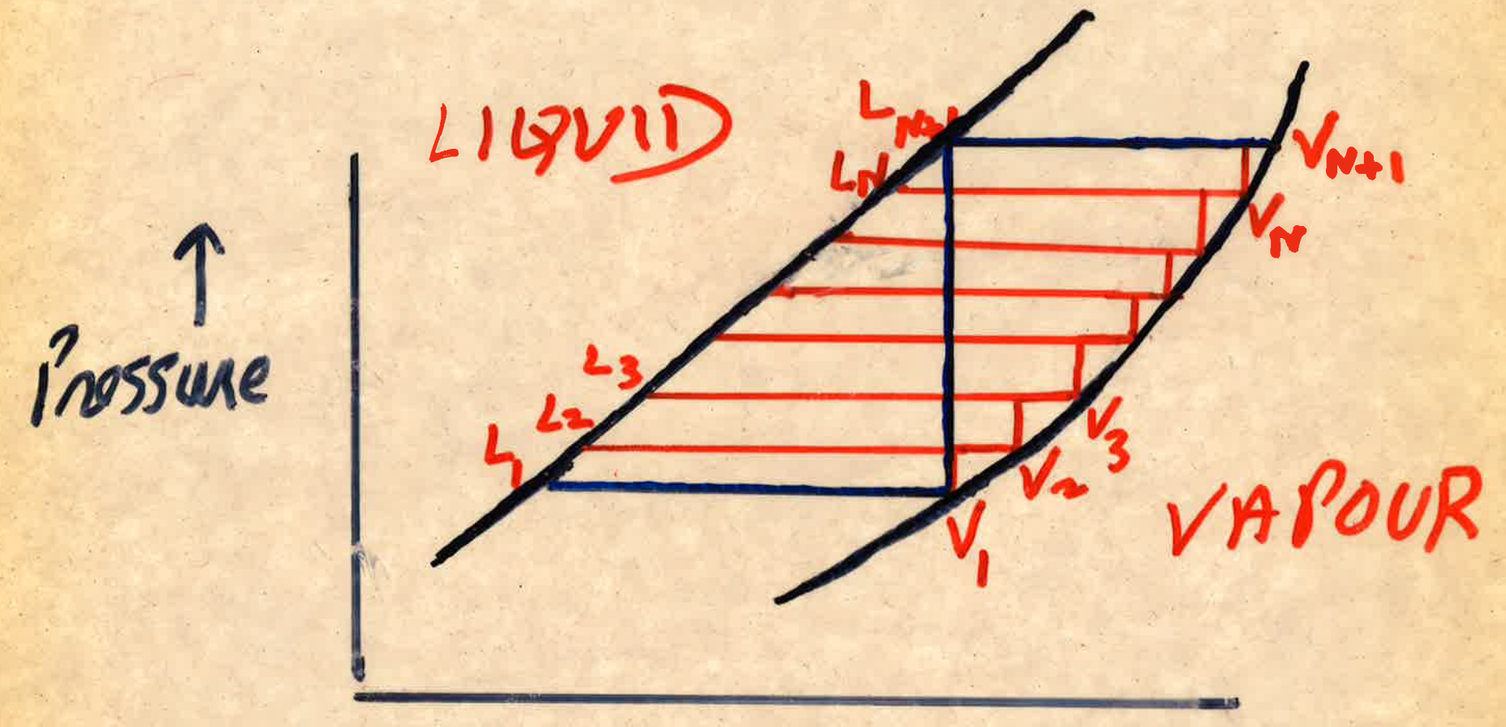


$$x_n = \frac{1}{1+R^n}, \quad y_n = \frac{1}{1+R^{-n}}$$

where $R = p_A / p_B$


LIQUID
Pressure
G
F
H
E
VAPOUR.
0
½
x
1

REVERSIBLE DISTILLATION



R.T.P. $\lim_{m,N\to\infty} \pi^{(m)}(L_1)=1$, $\lim_{m,N\to\infty} \pi^{(m)}(L_T)=0$ $\xrightarrow{X}$ $R=2,3\ldots N+1$

$\lim_{m,N\to\infty} \pi^{(m)}(V_{N+1})=1$, $\lim_{m,N\to\infty} \pi^{(m)}(V_T)=0$ $R=1,2\ldots N$

$$\Delta S_{sep}^{(n)}(k)$$

$$= -R\left[\frac{2}{1+k^n}\ln\left(\frac{2}{1+k^n}\right)\right.$$

$$+\frac{2}{1+k^{-n}}\ln\left(\frac{2}{1+k^{-n}}\right)+\frac{\ln k}{1+k^n}$$

$$\left.-\ln\left(\frac{1+k^{n-1}}{1+k^n}\right)+2\ln\left(\frac{1+k}{2k}\right)\right]$$

$$-\frac{1}{T(1+k^n)}\left(L_A+k^n L_B\right)$$

$R > 1$,

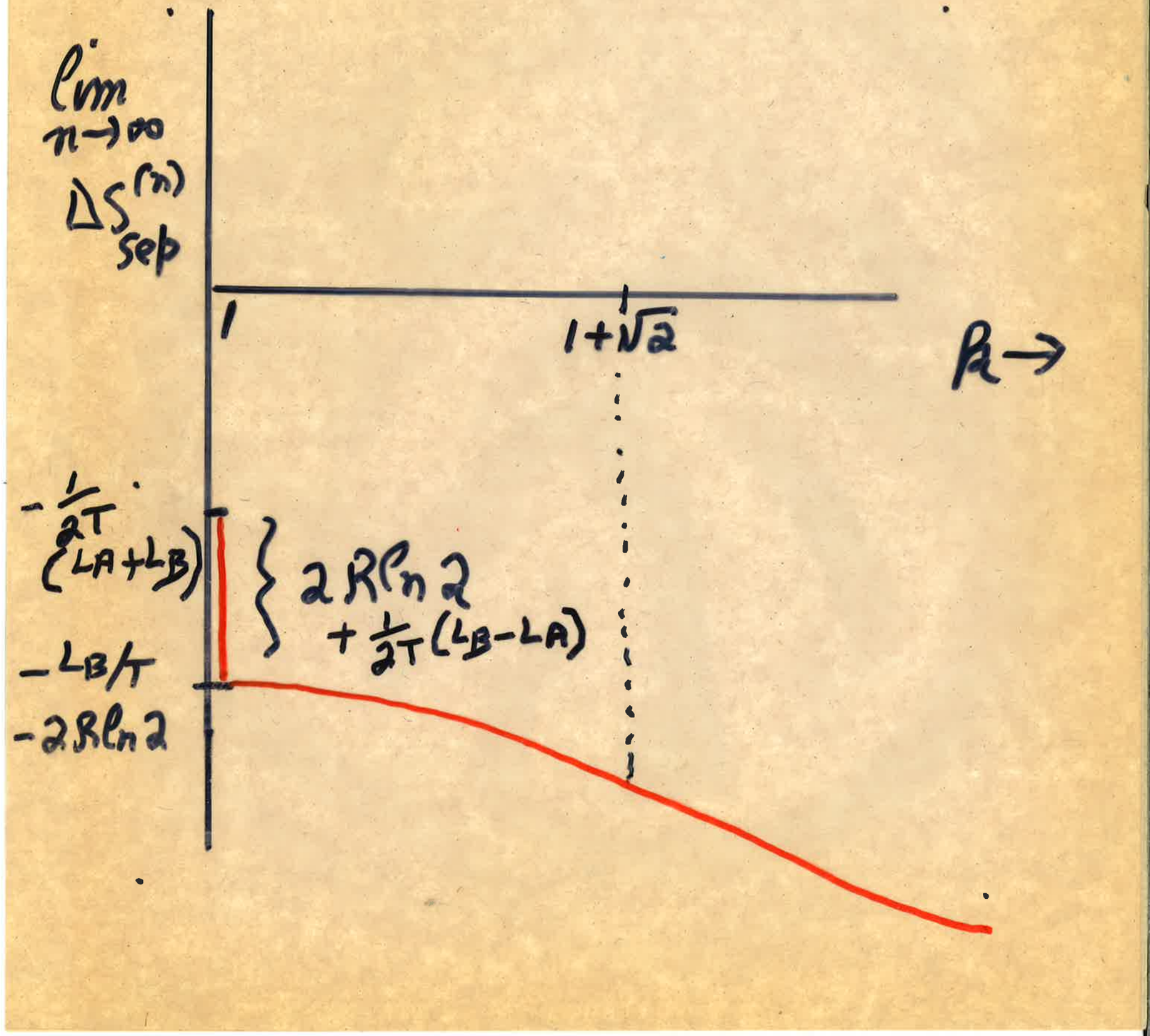
$$\lim_{n\to\infty} \Delta S^{(n)}_{sep}(R)$$

$$= -2R\ln 2 - L_B/T + R\ln\left(\frac{4R}{(1+R)^2}\right)$$

$R = 1$,

$$\lim_{n\to\infty} \Delta S^{(n)}_{sep}(R)$$

$$= -\frac{1}{2T}(L_A + L_B)$$


$\lim_{n\to\infty} \Delta S_{sep}^{(n)}$
1
$1+\sqrt{2}$
R →
$-\frac{1}{2T}(L_A+L_B)$
$-L_B/T$
$-2R\ln 2$
$2R\ln 2 + \frac{1}{2T}(L_B-L_A)$